PB81-213407

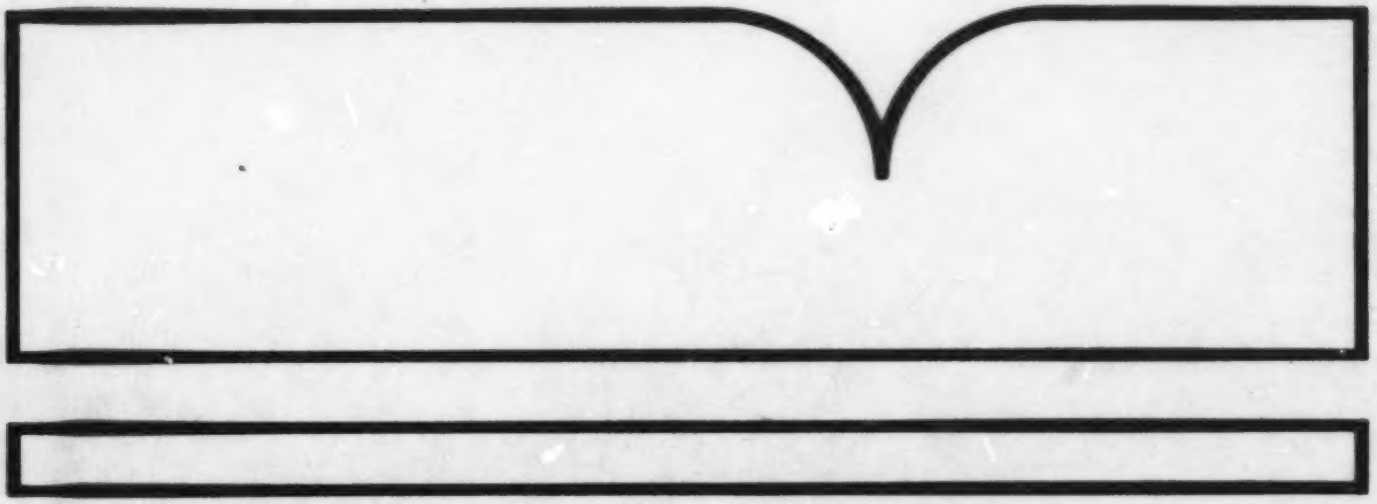
Determination of Dissolved Kepone by Direct Addition of XAD-2 Resin to Water

Virginia Inst. of Marine Sciences
Gloucester Point

Prepared for

Environmental Research Lab.
Gulf Breeze, FL

Jun 81



U.S. Department of Commerce
National Technical Information Service
NTIS

EPA-600/J-80-292
Journal Article

Determination of Dissolved Kepone by Direct Addition of XAD-2 Resin to Water

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Kepone (decachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*c*,*d*]pentalen-2-one), a chlorinated hydrocarbon pesticide, was manufactured at Hopewell, Va., from 1966–1975. Waste discharges contaminated the adjacent James River from Richmond to the Chesapeake Bay, producing adverse environmental and economic impacts (*1–3*).

Extraction techniques have been developed for the determination of Kepone in water, using benzene (*1*, *4*), toluene–ethyl acetate (*2*), or ethyl ether–hexane (*5*) as solvents, with detection limits ranging from 20–40 ng/L (*1*, *2*, *4*, *5*). However, because of insensitivity of these existing methods, concentration differences of a few parts-per-trillion (ng/L) dissolved Kepone may go undetected. Therefore, an analytical procedure was needed to quantify Kepone in water at concentrations of <20 ng/L.

In addition to solvent extraction, techniques for removing organics from water have involved the use of columns packed with porous XAD polymer resins (*6–10*). Columns of XAD-2 resin, a low polarity styrene–divinylbenzene copolymer with high sorptive capacity, have been used for the extraction of a wide variety of organics and pesticides from water (*7–9*). However, at least 5–10 h would be required for large volumes (>10 L) of water to pass through the resin columns in order to collect and quantify low levels of organics (*7*). Recovery efficiency could thus be adversely affected by possible interaction of these nanogram quantities of organics with the container walls or with other components in the reservoir containing water waiting to be eluted through the resin column. Therefore, to lessen the time delays of column elution for large volumes (>10 L) of water, yet retain the use of the highly sorptive polymer resins to collect nanogram quantities of organics, an analytical procedure was developed to quantify parts-per-trillion concentrations of Kepone by the addition of XAD-2 resin directly to water. To alleviate the problem of reduced XAD extraction efficiency from accumulation of suspended solid in the resin (*11*), water samples were vacuum filtered through a manifold filtration setup containing 0.8-μm Millipore filters. This filtration was necessary prior to XAD column elution to remove suspended solids and to quantify only "dissolved" Kepone, which is defined here as Kepone in water samples with no particles >0.8 μm.

To determine if Kepone could be adsorbing onto the Millipore filter, 20 L of distilled water containing 25 ng/L dissolved Kepone was passed through 0.8-μm Millipore filters. The filters were then Soxhlet extracted with 1:1 (v/v) diethyl ether/petroleum ether (*4*). No Kepone was detected (<0.3 ng/L). As another check, samples (20 L) of James River water, known to contain suspended and dissolved Kepone (*1*, *2*), were first continuously centrifuged, to collect suspended solids for Kepone analysis, then filtered through 0.8-μm Millipores. Even though dissolved Kepone concentrations were 5–10 ng/L, the Millipore filters yielded no detectable Kepone. Therefore, Kepone adsorption onto Millipore filters, before the addition of XAD-2 resin to the water, appears to be minimal. By subsequent direct addition of the XAD-2 resin to the filtered water, possible Kepone losses via reservoir adsorption or component interaction are minimized since time-consuming column elution for large volumes of water is eliminated and the resin comes in contact with dissolved Kepone in the 20 L of water within 1–3 h of sample collection.

EXPERIMENTAL

Apparatus. Analysis of the extracts for Kepone was carried out using a Tracor Model 222 gas chromatograph with an electron capture detector. The gas chromatographic conditions were: detector–electron capture (^{63}Ni) 350 °C, injector 220 °C, column 210 °C, carrier gas 95% argon/5% methane, flow: 80 mL/min. The column was 6 ft × 2 mm i.d. glass, 1.5% OV-17/1.95% QF-1 on 100/120 Chromosorb W HP.

Reagents. All solvents were chromatography grade, distilled-in-glass (Burdick and Jackson Laboratories). The 86.6% pure Kepone reference standard (Environmental Protection Agency, Research Triangle Park, N.C.) was used as supplied and stored in a desiccator. The XAD-2 polymer resin (Rohm and Haas) was purified by a 24-h Soxhlet extraction with methanol (*8*), and stored in methanol. Florisil (Floridin Co.) was kept in an oven at 135 °C.

Procedure. At least 20 L of York River water (19‰ salinity, pH 7.8) was prefiltered through 0.8-μm Millipore filters and collected in a polyethylene carboy. The carboy was placed on a magnetic stirrer, Kepone dissolved in acetone was added, and the water stirred for several minutes. Sixty grams of precleaned XAD-2 resin was added and the water and resin were stirred for at least 8 h. The water was then vacuum filtered through a Buchner funnel containing Whatman #1 filter paper (18.5 cm). The collected XAD-2 resin was placed in a 500-mL glass beaker on a magnetic stirrer, and stirred for 10 h with 200 mL 1:3 (v/v) toluene/ethyl acetate mixture. After vacuum filtering the resin–organic mixture and collecting the resin on Whatman #1 filter paper (9.0 cm), the resin was again extracted with 200 mL of 1:3 (v/v) toluene/ethyl acetate for 10 h. Each extract was then placed

Table I. Recovery of Kepone from Solution in Prefiltered York River Water Samples (20 L)

added, ng	concentration, ng/L	recovered, ng	recovery, %
0	<0.3[a]	<6[a]	-
102	5.1	94	92
109	5.5	95	87
132	6.6	116	88
215	11	191	89
215	11	210	97
294	15	268	91
			$\bar{x}$ = 90.7

[a] Minimum working detection limit for four determinations.

in a separatory funnel, and any aqueous layer removed. The remaining organic layers (volumes measured) were filtered through sodium sulfate (volumes again determined) to remove any traces of water. These extracts were concentrated under nitrogen at 70 °C to less than 5 mL. Each extract was eluted through a Florisil column to remove interfering organics (*4*), omitting the use of petroleum ether. The sequence of additions to the Florisil column was (a) 7 mL of solvent I (*n*-hexane containing 2% methanol, 4% benzene), (b) toluene–ethyl acetate extract from above, (c) 7 mL of solvent I, and (d) 30 mL of solvent II (*n*-hexane containing 1% methanol, 2% acetonitrile, 4% benzene). Kepone, collected in the solvent II from both extracts, was quantified on the gas chromatograph.

RESULTS AND DISCUSSION

Table I shows recovery of Kepone from solution in river water samples. York River water, with no Kepone added, was found to contain <0.3 ng/L, the minimum working detection limit. Recovery averaged 90.7 ± 3.8% (95% confidence, n = 6) for 5–15 ng/L of dissolved Kepone in the prefiltered river water.

This analytical procedure permits the determination of <15 ng/L of dissolved Kepone by maximizing the volume of water (20 L) which can be extracted with XAD-2 resin by direct addition of the resin to water, while lessening the time required before resin contact with the dissolved Kepone. Kepone losses due to container wall adsorption are minimized, as shown by recoveries recorded in Table I.

This procedure is presently being used to quantify dissolved Kepone concentrations of <15 ng/L in the James River and thus provide further information on its behavior in natural waters. Preliminary results show dissolved Kepone concentrations of 3.0–10 ng/L in the vicinity of Skiffes Creek along the James River. Other investigators have observed dissolved Kepone concentrations below their detection limits of 20–40 ng/L (*1*, *2*) up to 45 ng/L in the vicinity of Hopewell (*2*, *5*). Since our understanding of Kepone properties and behavior in natural waters is limited, this procedure to quantify dissolved Kepone can assist researchers in their attempts to calculate the migration and interaction of dissolved and particulate Kepone species in river water.

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RECEIVED for review October 29, 1979. Accepted January 7, 1980. The authors express their appreciation to the U.S. Environmental Protection Agency for partial funding of this work (Grant No. R804993-01-2) and to the Commonwealth of Virginia for the remainder. VIMS Contribution No. 929.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/J-80-292 ERL,GB 153	2. Journal Article
3. REC	PB81-213407
4. TITLE AND SUBTITLE Determination of Dissolved Kepone by Direct Addition of XAD-2 Resin to Water	5. REPORT DATE June 1981
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Richard L. Harris, Robert J. Huggett, Harold D. Slone	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Virginia Institute of Marine Science & School of Marine Science, College of William & Mary Gloucester Point, Virginia 23062	10. PROGRAM ELEMENT NO. C87E1A 11. CONTRACT/GRANT NO. R804993
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Office of Research and Development Environmental Research Laboratory Gulf Breeze, Florida 32561	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA-600/04

15. SUPPLEMENTARY NOTES

Analytical Chemistry, (1980), 52, 779.

16. ABSTRACT

Analytical procedures are described for the determination of Kepone in water, using benze, toulene-ethyl acetate, or ethyl ether-hexane as solvents. The procedure is presently being used to quantify dissolved Kepone concentrations of <15 ng/l in the James River and thus provide further information on its behavior in natural waters. Preliminary results show dissolved Kepone concentrations of 3.0-10 ng/l in the vicinity of Skiffes Creek along the James River.

benzene

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Biochemistry Pesticides	Kepone	

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NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT Release to public.	19. SECURITY CLASS (*This Report*) Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS (*This page*) Unclassified	22. PRICE

END

DATE

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7-29-81

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